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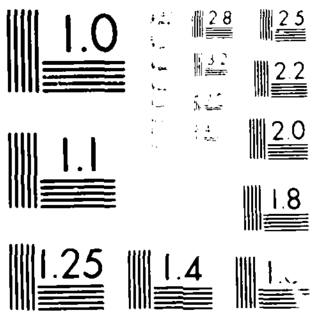
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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

SUMMARY

The quantitative analysis of hydrogen peroxide dissolved in microemulsions has been worked out for concentrations ranging from 8 to 10^{-7} M.

The stability of a O/W microemulsion containing lauryl acid sodium salt, cyclohexane, n-butanol and water towards hydrogen peroxide has been tested. Kinetic measurements have been made for oxygen evolution as well as the consumption of hydrogen peroxide.

Enhanced oxidation of N-methyl-phenothiazine with singlet oxygen has been found in a O/W microemulsion containing sodium lauryl sulfate, cyclohexane, n-butanol and water.

SHORT TERM PROJECTS

New O/W and W/O microemulsions containing tert-butanol instead of n-butanol will be worked out and tested for their stability against hydrogen peroxide.

Mechanistic interpretations of the oxidation reaction involving hydrogen peroxide and concerning the - hypothetic - intermediate production of superoxide will be verified using specific trapping agents.

Infrared measurements of the singlet oxygen emission in O/W microemulsions will be necessary in order to elucidate reasons for the enhanced photochemical oxidation of N-methyl-phenothiazine.

Some of the topics studied qualitatively and reported in the first periodic report have been selected with first priority for a detailed and fundamental investigation:

1. Enhanced oxidation reactions in microemulsions using hydrogen peroxide

The system lauryl acid sodium salt, cyclohexane, n-butanol, water has been selected as one of those potentially compatible microemulsions for transparent and fluid mixtures with perfluorinated microemulsions in corresponding O/W and W/O regions (1). Its pseudo-ternary phase diagram has been established and is shown in figure 1.

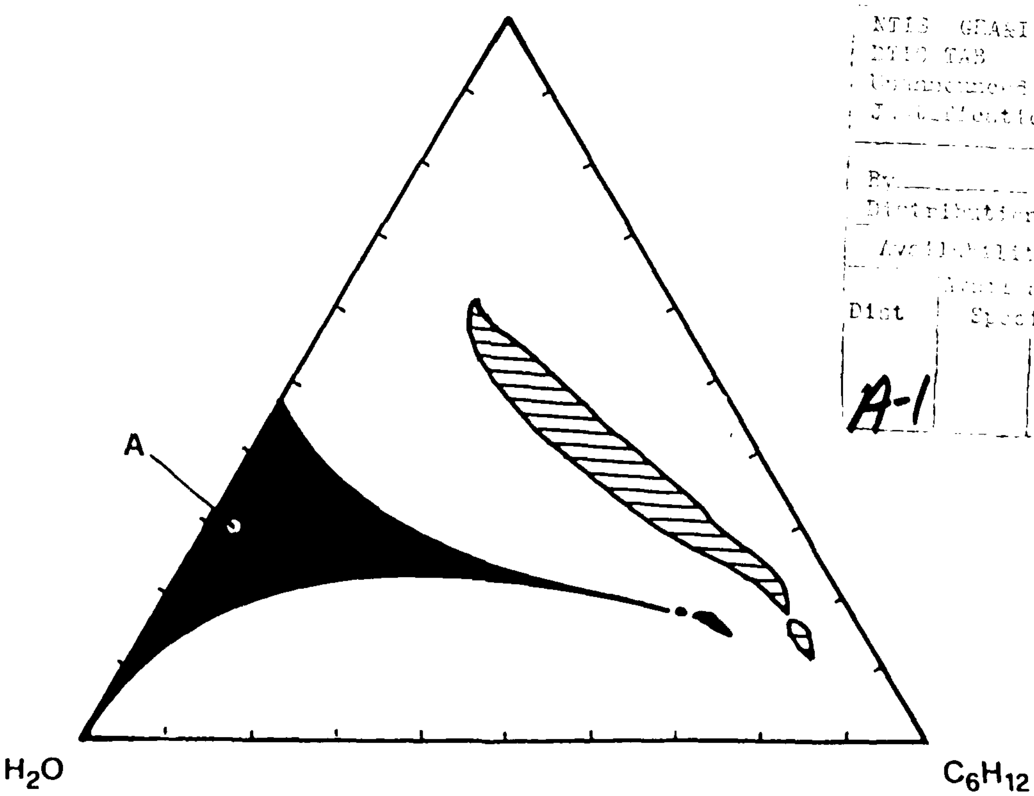

Figure 1. - Pseudo-ternary phase diagram of the system lauryl acid sodium salt, cyclohexane, n-butanol, water

1.1. Stability of the O/W microemulsion of lauryl acid sodium salt, cyclohexane, n-butanol and water against hydrogen peroxide

Hydrogen peroxide is a widely used oxidant for oxidative bleaching in textile industry (2). Used in microheterogeneous systems, oxidation reactions could be enhanced by a better dissolution of organic (fatty, hydrophobic) substances.

Qualitative evidence of such an enhancement of oxidation reactions in microheterogeneous systems, i.e. microemulsions, calls for a series of investigations which by themselves are of great interest for the further development of the general theme:

- quantitative analysis of hydrogen peroxide in microheterogeneous systems
- thermal stability of microemulsions against hydrogen peroxide, kinetic investigations of oxidation and decomposition reactions
- kinetic studies and product determination of oxidation reactions of solubilized organic material.

At the present state, we have succeeded in developing methods of quantitative analysis of hydrogen peroxide at high concentrations ($> 10^{-4}$ M) as well as low concentrations (10^{-4} to 10^{-7} M). By means of measuring oxygen evolution and consumption of hydrogen peroxide, we further evaluated the stability of a given microemulsion (figure 1, point A).

1.1.1. Quantitative analysis of hydrogen peroxide ($> 10^{-4}$ M) in a O/W microemulsion

High concentrations of hydrogen peroxide ($> 10^{-4}$ M) can be titrated with aqueous potassium permanganate (10^{-1} N). The microemulsion is destroyed upon addition of 20% sulfuric acid (10 ml for 10 ml of the hydrogen peroxide containing microemulsion). Titration is performed at room temperature. Mn^{2+} catalyzed decomposition of hydrogen peroxide leads after a period of initiation to a fast titration with a rather low limit of error (5%). Doubts about this method of analysis because of a potential parallel oxidation of n-butanol or of butyraldehyde contained in the microemulsion can be rejected. In fact, secondary oxidation reactions of this type are much slower and do not affect the result. This point has been investigated in some detail by comparing results of the potassium permanganate titration with those of the DPD method (s. 1.1.2.).

1.1.2. Quantitative analysis of hydrogen peroxide (10^{-4} to 10^{-7} M) in a O/W microemulsion

For lower concentrations of hydrogen peroxide (10^{-4} to 10^{-7} M), the titration with potassium permanganate is substituted by the DPD method known from water chemistry (3). In this analytic reaction hydrogen peroxide oxidises N,N-dimethyl-phenylene-1,4-diamine (DPD) in the presence of peroxidase as a catalyst. The resulting red coloured solution may be analysed spectrophotometrically after a standard curve has been previously established.

Figure 2 shows the standard curve of the absorption at 552 nm versus hydrogen peroxide concentration. Its error at zero concentration is 3×10^{-3} (A), and the linearity ist better than 98%. This leads to an average reproducibility with an error of about 2,5%, and, in combination with the permanganate titration, to a maximum error of the analytic method of 8%. This precision ist satisfactory for the kinetic investigations planned as described above.

The following analytic procedure has been adopted:

25 ml of the hydrogen peroxide containing microemulsion are buffered with 3 ml of a 0,5 M phosphate buffer (pH = 6,8), then 0,1 ml of a freshly (daily) prepared DPD solution (100 mg of DPD in 10 ml of 0,1 N sulfuric acid) are added. Finally, peroxidase (10 mg in 10 ml

of water) is added (50 µl), and the mixture is stirred and (partially) transferred into a spectrophotometric cell. The absorption is measured at 510 and 552 nm after a fixed period of time measured from the moment of peroxidase addition, e.g. 90 s.

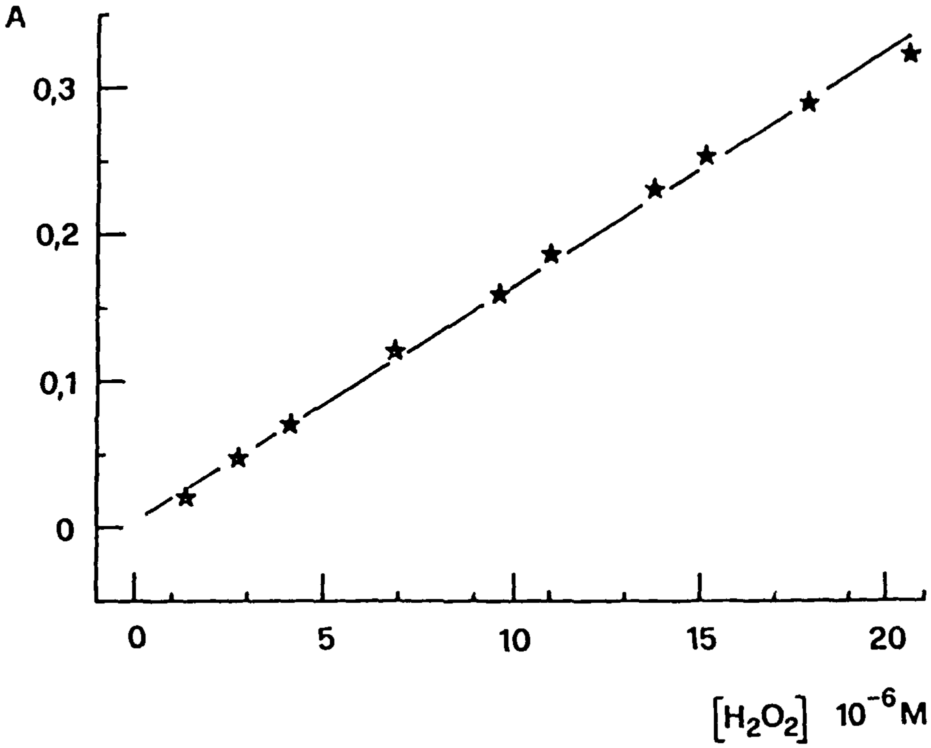

Figure 2. - Standard curve of the absorption of oxidised DPD versus concentration of hydrogen peroxide

The combination of the two methods of analysis provides the possibility to follow the consumption of hydrogen peroxide during oxidation reactions almost until their completeness.

1.1.3 Thermal stability of the O/W microemulsion in the presence of hydrogen peroxide

Based on our experience of hydrogen peroxide oxidations of cotton and cellulose (2), we estimated that a similar oxidation of n-butanol contained in microemulsions must be rather slow. Such oxidation reactions are usually accompanied by a substantial oxygen evolution, and we decided to follow the kinetics of the n-butanol oxidation by a gasometric measurement of the produced oxygen as well as by the analysis of the remaining hydrogen peroxide. Figure 3 shows the oxygen evolution of the kinetic experiments performed at 15^{0}C.

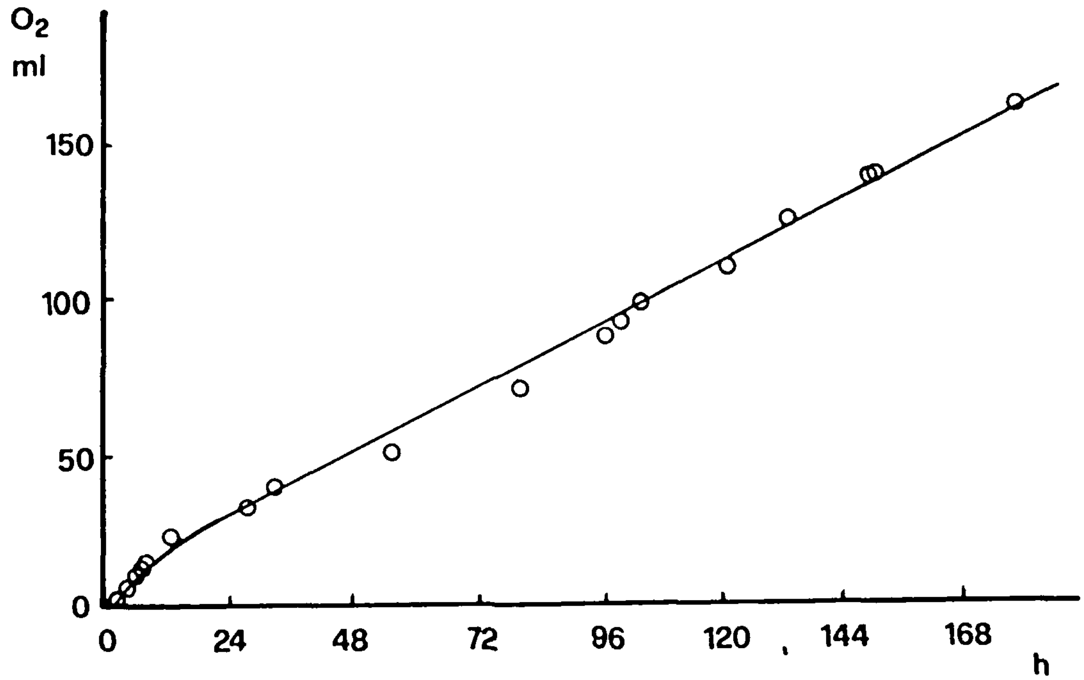

Figure 3. - Oxygen evolution during the oxidation of n-butanol in a hydrogen peroxide containing O/W microemulsion (30% hydrogen peroxide with the water added)

It is interesting to note:

- the period of initiation
- the calculated ratio of hydrogen peroxide consumed versus oxygen produced is about 3

At this state, it is too early to present any mechanistic interpretation, although, there is some evidence that superoxide might be one of the reactive intermediates.

Similar microemulsions using tert-butanol as a cosurfactant have

have just been found and are currently under investigation.

2. Enhanced oxidation reactions in microemulsions using singlet oxygen

Starting from the mechanistic hypothesis of Foote and Peters (4) for the sensitized photooxidation of sulfides:

$$ {}^{1}_{0}\mathrm{Sens} \longrightarrow {}^{1}_{1}\mathrm{Sens} \qquad (1)$$

$$ {}^{1}_{1}\mathrm{Sens} \longrightarrow {}^{3}_{1}\mathrm{Sens} \qquad (2)$$

$$ {}^{3}_{1}\mathrm{Sens} + O_2 \longrightarrow {}^{1}_{0}\mathrm{Sens} + {}^{1}O_2 \qquad (3)$$

$$ {}^{1}O_2 + R_2S \longrightarrow R_2SO_2 \qquad (4)$$

$$ R_2SO_2 + R_2S \longrightarrow 2\ R_2SO \qquad (5)$$

$$ {}^{1}O_2 + R_2S \longrightarrow O_2 + R_2S \qquad (6)$$

$$ {}^{1}O_2 \xrightarrow[\text{solvent}]{} O_2 \qquad (7)$$

a higher local concentration of sulfide should enhance the rate of the dismutation of the intermediate peroxide (reaction 5).

In fact, the results of the kinetic experiments show this enhancement of the sulfoxide production in a O/W microemulsion; both, the photosensitized oxidation of N-methyl-phenothiazine in methanol an in a W/O microemulsion are slower by factors of 2 and 3,5, respectively (figure 4).

The compositions of the microemulsions used are indicated in the pseudo-ternary phase diagram shown in figure 5.

We conclude from our calculations, based on spectrophotometric measurements of product formation and electrochemical measurements

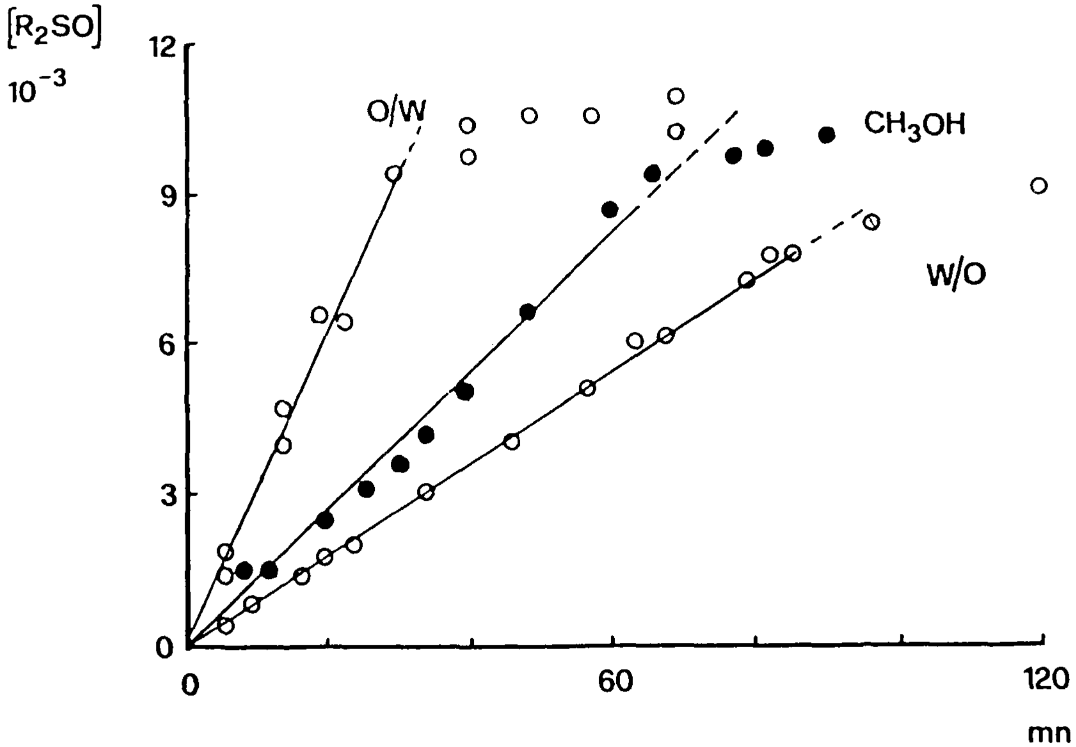

Figure 4. - Kinetics of photosensitized sulfoxide formation of N-methyl-phenothiazine in fonction of the medium

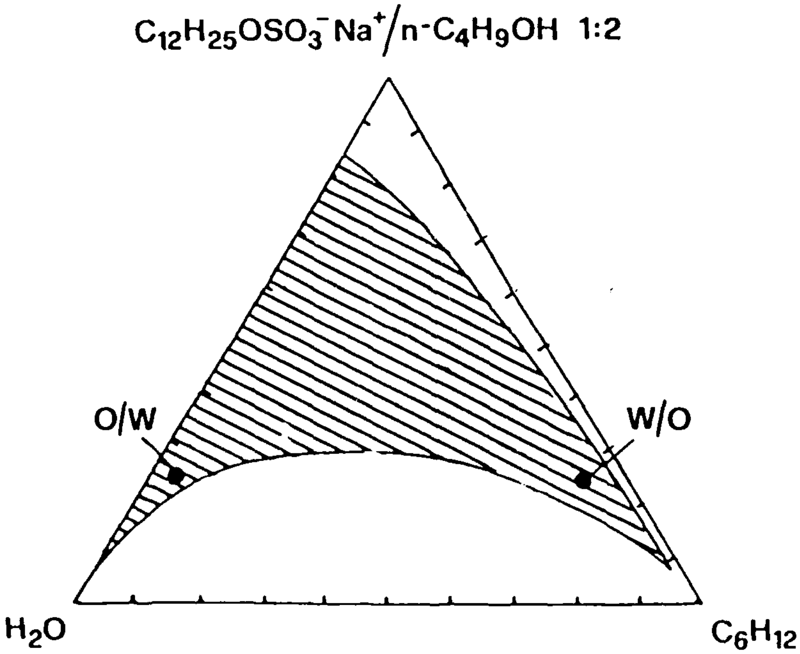

Figure 5. - Pseudo-ternary phase diagram of the system sodium lauryl

of oxygen consumption (5), that the low quantum yield of the photo-oxidation in methanol and in the W/O microemulsion is due to an efficient physical quenching of singlet oxygen by the substrate (reaction 6). In the O/W microemulsion, however, deactivation of singlet oxygen by the solvent (reaction 7) is predominant. The variation of the rates of those two reactions in function of the medium cannot be explained by the fact that reaction 7 is twice as fast in water than in methanol. In fact, the efficiency of the physical quenching (reaction 6) requiring complex formation between singlet oxygen and the substrate and subsequent dissociation of the two ground state molecules could be reduced by the competitive reaction of the complex producing the intermediate peroxide. This competitivity could be enhanced by a reduction of the corresponding activation entropy (6); previous work has shown that high local concentrations of substrate and subsequent agregation may lead to a substantial reduction of the redox potential (7). A similar effect would lead in this case to a higher reactivity of the substrate for electron transfer and subsequent recombination of radical ion pairs and, thus, to an overall enhancement of the electrophilic addition of singlet oxygen.

These experiments are currently completed by measurements of the infrared emission of singlet oxygen under similar experimental conditions in order to differentiate between the rate of reaction 7 and those of reactions 4 and 6.

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A. B.

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